

The effect of doping on the microhardness behaviour of anthracene

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Received 13 April 1998, accepted 5 May 1998

Abstract : Microindentation hardness studies using the Vickers and Knoop indenters were carried out on single crystals of anthracene doped with carbazole and phenanthrene respectively. It is observed that the Vickers hardness *versus* load curve exhibits two peaks at 55 g and 90 g loads with hardness values of 5.4 kg/mm² and 7.9 kg/mm² respectively, for carbazole doped anthracene, whereas the Knoop hardness variation with load for phenanthrene doped anthracene is a curve with two peaks at loads 2.5 g and 7.5 g with hardness values 13.5 kg/mm² and 12.4 kg/mm² respectively. The Vickers hardness behaviour is explained in terms of the ease of slip of the (100) plane in comparison to the (20 $\bar{1}$) plane in pure anthracene. The Knoop hardness behaviour is explained in terms of the splitting of the (20 $\bar{1}$) [010] type of dislocations in phenanthrene doped anthracene.

Keywords : Microhardness doping, anthracene

PACS Nos. : 81.40.Np, 62.20.Fe

1. Introduction

Impurities change the physical properties of any substance. The process of intentionally introducing impurity atoms to obtain a desired change in any physical property such as conductivity is called doping [1]. A most common example is that of semiconductors like silicon or germanium in which the extrinsic conductivity can be adjusted over a wide range by additions of group III and group V compounds.

It has been suggested that impurity atoms are attracted to dislocations [2,3]. At an edge dislocation, large impurity atoms would be attracted to the expanded region below the glide plane where there is more room for them. Small substitutional impurity atoms would be attracted to the region above the glide plane. The segregation of impurities at a

dislocation, effects the mechanical properties because its movement is hindered or eased by the impurities. The segregation of impurities at a dislocation will lead to different chemical properties of a crystal near a dislocation as compared to a normal part of the crystal [4]. The fact that the energy associated with an impurity atom is affected by its proximity to a dislocation causes the impurity concentration to change in the vicinity of a dislocation line [5].

Additions of one metal to another result in a steady increase in hardness until a saturation is obtained and two phased structures are caused due to further increase of the solute. Various elements with solid solubilities on aluminium have shown a relationship between hardness and concentration of solute [6].

There does not exist literature on the microhardness behaviour of the addition of an organic molecular compound with another to the best of the authors' knowledge.

2. Experimental and results

2.1. Crystal growth :

Single crystals of carbazole doped anthracene and phenanthrene doped anthracene were grown from the melt by the Bridgmann method. The starting material was column chromatographed, twice vacuum sublimed and zone refined. The material was transferred to the crystal growth tubes without exposure to the atmosphere [7]. The crystals were cleaved in the usual manner using a sharp blade. Smooth cleavages were selected after optical examination.

2.2. Microhardness :

The crystals were indented on a Carl Zeiss NU 2 Universal Research Microscope. The indents were made with Vickers and Knoop indenters. A number of indents were made at a particular load. The average length of diagonals was used in calculating the Vickers hardness number (H_v) using the formula :

$$H_v = 1.8544 \times P / d^2 \quad (1)$$

and the long diagonal length was used in calculating the Knoop hardness number (H_k) using the formula :

$$H_k = 14228.8 \times P / d^2, \quad (2)$$

where P is the applied load in grams and d , the mean diagonal length in micrometers. The indentation time of 10 s was kept constant as this time was adequate to minimize the vibration effects on the results. The crystal size was much larger than the indentation size, thus eliminating the boundary effects on the results. The distance between the indents was five times the size of the largest indentation mark. The crystal thickness was relatively

large such that the indenter did not sense the lower surface [6]. A number of crystals were indented.

Figure 1 shows the Vickers hardness variation with load curve for pure anthracene single crystals [8]. The plot shows two peaks at 30 g and 67 g loads having hardness values 7.2 kg/mm² and 4.95 kg/mm² respectively.

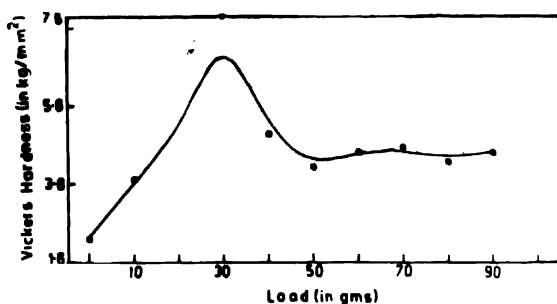


Figure 1. The best fit plot of Vickers hardness *versus* load for pure anthracene single crystals

Figure 2 is the Knoop hardness *versus* load plot which also reveals two peaks but at lower loads, 5 g and 17.5 g [9]. These peaks have higher hardness values 13.0 kg/mm² and 11.4 kg/mm² respectively.

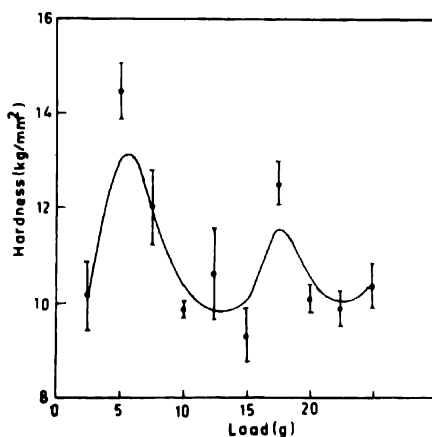


Figure 2. The best fit curve of Knoop hardness variation with load for pure anthracene single crystals

Figure 3 shows the result of Vickers hardness studies performed on carbazole doped anthracene single crystals. The hardness *versus* load curve reveals two peaks at 55 g and 90 g having hardness values 5.4 kg/mm² and 7.9 kg/mm² respectively.

Knoop hardness studies were carried out on phenanthrene doped anthracene. Figure 4 is the curve of hardness variation with load which shows two peaks at loads 2.5 g and 7.5 g with hardness values 13.5 kg/mm² and 12.4 kg/mm² respectively.

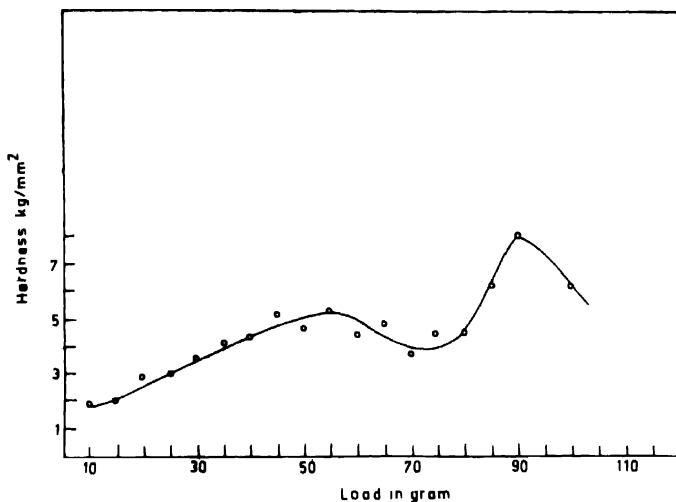


Figure 3. The best fit curve of Vickers hardness variation with load for crystals of carbazole doped anthracene

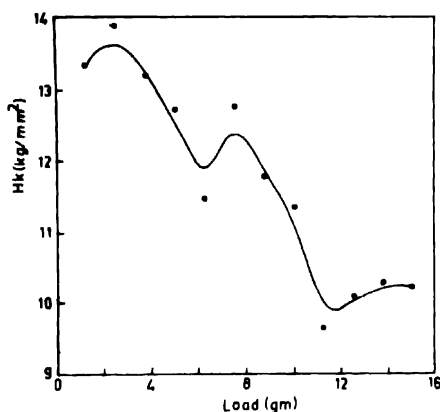


Figure 4. The best fit plot of Knoop hardness versus load for phenanthrene doped anthracene single crystals.

3. Discussion

Anthracene crystallizes in the monoclinic structure. The lattice parameters are $a = 8.562 \text{ \AA}$, $b = 6.038 \text{ \AA}$ and $c = 11.184 \text{ \AA}$ with $B = 124^\circ 7'$. The compound has the structural formula $C_{14}H_{10}$ with two molecules per unit cell. The space group is $P2_1/a$ and it cleaves along the (001) plane [10].

Phenanthrene crystallizes in the monoclinic structure. Its lattice parameters are $a = 8.660 \text{ \AA}$, $b = 11.500 \text{ \AA}$ and $c = 19.240 \text{ \AA}$ with $B = 98^\circ 4'$ with space group $P2_1/a$. The compound has the structural formula $C_{14}H_{10}$ with two molecules per unit cell. Phenanthrene cleaves along the (001) plane [10].

Carbazole belongs to the orthorhombic structure. Its structural formula is $C_{12}H_9N$ and it has four molecules per unit cell. The space group is $P2_{1nm}$ and it cleaves along the (010) plane. The lattice parameters are $a = 7.772 \text{ \AA}$, $b = 19.182 \text{ \AA}$ and $c = 5.725 \text{ \AA}$ with $\alpha = \beta = \gamma = 90^\circ$ [11].

In case of pure anthracene, the molecules are tightly entangled across the adjacent (0k0) planes. The first peak in the Vickers hardness *versus* load plot of Figure 1 corresponds to slip taking place on $(20\bar{1})$ plane and second peak corresponds to slip on (100) plane. Thus, on indenting at low loads, dislocations of the type $(20\bar{1})$ [010] are generated whereas at higher loads, the (100) [010] type of dislocations are activated.

The plot of Vickers hardness variation with load for carbazole doped anthracene of Figure 3 shows that the peak positions have been interchanged as compared to Figure 1. Also they occur at higher loads and the hardness values are 5.4 kg/mm^2 and 7.9 kg/mm^2 compare well with the observations on pure anthracene crystals but interchanged.

The carbazole molecule is very similar to the anthracene molecule and goes in substitutionally in the lattice of anthracene. This reverses the plot of variation of hardness with load in the carbazole doped anthracene. The first peak appears at 55 g load with a hardness value of 5.4 kg/mm^2 which compares well with the hardness value of 4.95 kg/mm^2 at 67 g load in pure anthracene. Both (100) and $(20\bar{1})$ slip planes are facile but the $(20\bar{1})$ plane is more facile since it contains the molecular axis and is the second most closely packed plane. Slip in the $(20\bar{1})$ occurs more readily along the [010] direction. Carbazole dilates the lattice causing the (100) slip plane to be more facile than the $(20\bar{1})$ slip plane. Thus, the movement of dislocations of the type $(20\bar{1})$ [010] are restricted due to the carbazole impurity while movement of dislocations of the (100) [010] type are facilitated. The nearly same hardness values at peak positions support these observations.

The Knoop hardness behaviour of pure and phenanthrene doped anthracene as shown by Figures 2 and 4 is very similar except that the peaks in the doped crystals appear at low loads in comparison to pure anthracene. The hardness values at the peaks are nearly the same within experimental error. The splitting of the $(20\bar{1})$ [010] dislocations into partials has been suggested in the case of pure anthracene. Similar behaviour is suggested in case of doped crystals, as phenanthrene substitutes for anthracene in the lattice the compounds have the same chemical formula except for a change in the shape of the molecule. Thus, it is concluded that doping pure anthracene crystals with phenanthrene dilates the lattice causing deformation to take place at much lower loads.

4. Conclusions

- (i) Anthracene and carbazole doped anthracene belong to the monoclinic system, having space group $P2_1/a$ with two molecules per unit cell. They deform in a similar manner as seen by the variation of hardness *versus* load plots of Figures 1 and 3 when indented on (001) cleavage surface.
- (ii) Carbazole is known to go in substitutionally in anthracene causing the lattice to relax, reversing the behaviour of hardness *versus* load.
- (iii) The movement of dislocations of the type $(20\bar{1})$ [010] are restricted due to the carbazole impurity while movement of dislocations of the (100) [010] type are facilitated. The hardness values at peak positions support these observations as well as the peaks appearing at higher loads.
- (iv) Knoop hardness studies on pure anthracene show two peaks in hardness *versus* load plot. These are due to the $(20\bar{1})$ [010] dislocations splitting into partials.
- (v) The Knoop hardness behaviour of pure and phenanthrene doped anthracene is very similar except that the peaks in the doped crystals appear at low loads as compared to pure anthracene. The hardness values at the peaks are nearly the same within experimental error, thus dilating the anthracene lattice.
- (vi) Splitting of $(20\bar{1})$ [010] dislocations into partials is also suggested in case of doped crystals as phenanthrene substitutes for anthracene in the lattice.

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